

Covalent Bonding Outline

KotzVSEPRoutline.doc

Covalent bonding is the sharing of two or more electrons between atoms of similar electron attraction.

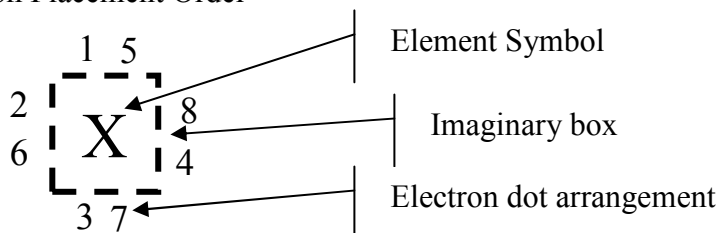
Covalent bonding occurs primarily between nonmetals

Covalent Bonding

- Generally between nonmetals
- Electrons are shared to achieve a stable octet.
- Usually takes place between valence electrons (outermost s and p sublevel electrons)
- Lewis Dot Structures - Provide a method of visualizing the valence electrons for an atom.

Writing Lewis Dot Structures for isolated atoms

Electron Placement Order



Writing Lewis Structures for Molecules

1. Determine the most likely arrangement of atoms.
 - a. Least EN atom is usually in the center.
 - b. Molecules are often symmetrical.
 - c. Hydrogen is never a central atom and can only have a “duet”.
2. Determine the total number of valence electrons the molecule possesses.
3. Fill in the "octets" of the outer atoms (Place electrons in pairs around the outer atoms)
4. Check for an octet on the central atom.
 - a. If the central atom has an octet and there are no leftover electrons, then you are done.
 - b. If the central atom doesn't contain an octet, consider a double or triple bond (two or three pairs of electrons shared between atoms)
 - c. If there are electrons left over, place them as lone pairs on the central atom.

Notes:

- Sometimes a line is used between atoms to represent a pair of electrons.
- The Lewis Dot Structure doesn't tell you anything about the geometry of the molecule.

Electronegativity is a value assigned to atoms that gives a sense of the relative tendency for an atom to draw electrons towards it. These values were developed by Linus Pauling. The most electronegative elements are the nonmetals in the upper-right corner of the periodic table (F, O, N, Cl) and the least electronegative are the metals in the lower-left corner (Cs, Fr, etc.). A high positive value indicates a high attraction for electrons in a bond and a low (or fractional) number indicates a relatively low attraction.

Fluorine at 4.0 has the highest electronegativity and cesium/francium at 0.7 have the lowest. The noble gases are not assigned electronegativity values for reasons which will become apparent.

The question arises, **what would make an atom attracted to an electron and why does it primarily happen to nonmetals?**

The answer lies in the configuration of the electrons around the atom and the energy associated with that arrangement. Recall that the quantum model of the atom has electrons filling energy levels (the n number) and sublevels (the l number). The **valence** electrons are the s and p electrons in the outermost energy level of that atom. These are the ones that primarily take part in the bonding process. If you notice, all noble gases have filled s and p sublevels (except He which only has an s sublevel). With 2 electrons in the s sublevel and 6 electrons in the p orbitals, there are a total of 8 electrons which chemists refer to as an **octet**. This octet of valence electrons is a very stable arrangement and one that most elements would like to "mimic" when possible. By attracting (or losing) electrons, elements can achieve a "noble gas" configuration of electrons and thus become more stable. It is important to remember that they don't become noble gases, they just have the same electron configuration. By doing this they become more stable.

Every time you add or remove an electron from an atom, it becomes more difficult to add or remove the next one, so whether or not an atom gains or loses electrons is largely a matter of its location of the periodic table relative to the noble gases. As a rule, **an element will attempt to achieve the electron configuration of the noble gas nearest to that atom on the periodic table**. Metals are generally closer to the previously occurring noble gas so they lose electrons. Nonmetals are closer to the next occurring noble gas and so will attempt to gain electrons to fill its octet. Since free electrons aren't usually just floating around waiting to be picked up by an atom, where is an element supposed to find one? The answer lies in the sharing of electrons between nonmetallic elements.

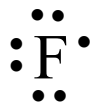
In a bond between two nonmetals, it is not beneficial for either one to lose an electron, so an ionic compound (i.e. the transfer of electrons) is not expected. Instead, two atoms will share their electrons such that each atom believes that the shared electrons are its own. This sharing is the covalent bond.

By sharing the correct number of electrons, each element can achieve the "octet" of a noble gas. NOTE: The elements in the bond will not necessarily have the electron configuration of the same noble gas, but will have the configuration of one of the noble gases.

Electron Dot Structure:

The electron dot structure was developed by G.N. Lewis as a way of visualizing the valence electrons in an atom to help determine how it will bond with other atoms. The electron dot structure is written by simply writing the symbol for the element and then placing its s and p **valence electrons** around the outside of the atom. Electrons are placed around the sides of an imaginary box surrounding the symbol, with filled orbitals written as pairs of dots and unfilled orbitals written as single dots. Each side of the box can have up to 2 electrons for a total of 8 for all sides.

For instance, the LDS for fluorine is



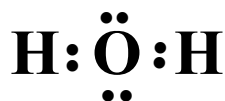
and for nitrogen it is



Examples:

1. Draw the Lewis dot structures for O, C, Li, H and Ar
2. Explain why fluorine is diatomic.
3. Describe the bonding between diatomic oxygen, and nitrogen and determine the number of electrons shared between each element.

A water molecule would be represented as follows:



Note that the oxygen "sees" eight electrons and the hydrogen only two (because of helium's configuration). Can you tell how many electrons are contributed by each atom?

Pairs of electrons that don't take part in bonding are known as **nonbonding pairs** or **lone pairs**. Pairs of electrons that take part in bonding are bonding pairs and are sometimes represented as a line between the atoms instead of drawing the dots. Sometimes more than one bond will form between two atoms so that an octet can be achieved.

The greater the number of bonds, the shorter the distance between the atoms. They tend to get "pulled" closer together.

In bonds between atoms of different electronegativities, the electron cloud is shifted towards the more electronegative atom and the molecule is said to be **polar covalent**. As the difference between the electronegativities gets greater and greater a point is reached where the bond is considered to be ionic. Purely (nonpolar) covalent bonds must have the same electronegativities. Sometimes polarity can be cancelled out by the geometry of the molecule which we will later see.

A difference in electronegativities of **1.7** or greater is considered to be ionic.

There are a set of rules for writing the Lewis Dot Structure for atoms that should be followed. Be sure to refer to these rules when solving complex molecular structures. Also, you should realize that the Lewis Dot Structure only gives the arrangement of the electrons around the atoms. It tells you nothing about the actual geometry of the molecule.

Examples:

Write the Lewis Dot Structure for the following species:



Formal Charge:

When more than one legitimate arrangement of the atoms in a Lewis dot structure are possible, chemists rely on what is known as the formal charge on each atom to ascertain the most likely arrangement. The formal charge should not be thought of as an actual "charge" on the atom per se, but rather a book keeping method for deciding between different plausible structures and the electronegativity of the atoms involved.

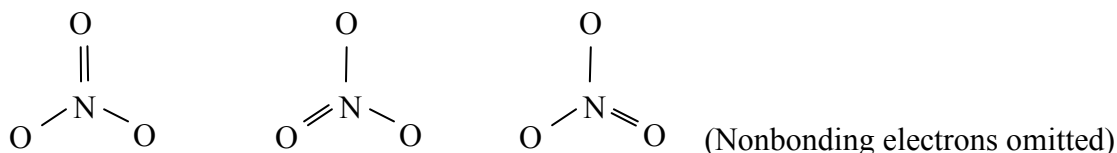
The equation is:

$$\text{Formal Charge} = \text{Total valence electrons} - \text{nonbonding electrons} - \frac{1}{2} \text{bonding electrons}$$

This should not be confused with the ionization state of atoms in an ionic compound where the more electronegative atom is assigned all of the bonding electrons.

Resonance Structures:

As you have seen from drawing LDS for different species, sometimes multiple bonds are required to fulfill the octet of the bonding atoms. A maximum of three bonds can occur between any two atoms and no more. When identical multiple bonding conditions can occur between two atoms (i.e. if say nitrogen can create a multiple bond between more than one possible oxygen atom in a symmetrical arrangement), the molecule is said to be in resonance. In reality, a portion of the multiple bond is shared between each of the bond pairs. The **bond order** gives the amount of bonding that occurs between two atoms. For instance, in the NO_3^- polyatomic ion, three different equivalent structures are possible:



Therefore the bond order between the nitrogen and each oxygen is $1 \frac{1}{3}$. The double bond is shared equally between the different atoms.

Exceptions to the octet rule:

Some molecules violate the octet rule. For instance B can bond with 3 atoms to have 6 pairs of electrons and other atoms (like in SF_6) have more than eight electrons (**expanded octets**) around the central atom. Also, any "leftover" pairs are always placed on the central atom. Periodically a molecule may have single, unpaired electrons. These are known as **free radicals** and are extremely reactively and potentially harmful to human beings.

Terms:

Enthalpy of sublimation, ΔH_{subl} : *The quantity of heat required to vaporize a given quantity of a solid at constant temperature. It is equal to the sum of the enthalpies of fusion and vaporization.*

Standard enthalpy of formation, ΔH_f° : *The enthalpy change that occurs in the formation of 1 mol of a substance in its standard state from the reference forms of its elements in their standard states. The reference forms of the elements are generally their most stable forms at the given temperature and 1 atm (or more recently 1 bar [1 atm = 1.01325 bar]) of pressure.*

Bond dissociation energy, D: *The quantity of energy required to break one mole of a particular covalent bond of a gaseous species.*

Ionization energy, IE: *The energy required to remove the least tightly bound electron from a ground-state atom (or ion) in the gaseous state.*

Electron affinity, EA: *The energy change that occurs when an electron is added to an atom in the gaseous state.*

Lattice energy: *The enthalpy change that accompanies the formation of one mole of an ionic solid from its gaseous ions.*

Atomic Radius: *The measure of the size of an atom based on the measurement of internuclear distances.*

Electronegativity, EN: *A measure of the tendency of an atom of a particular element in a molecule to attract bonding electrons towards itself. This is a relative, dimensionless scale developed by Linus Pauling. Note that the nitrogen (3.0), oxygen (3.5) and fluorine (4.0), three of the most electronegative elements (along with chlorine at 3.0) are the atoms responsible for hydrogen bonding.*

Coordinate covalent bond: *A covalent bond between two atoms in which one atom provides both of the electrons of the shared pair.*

Energy Changes in the Formation of Ionic Compounds:

When determining the standard enthalpy of formation for ionic compounds using the Born-Haber multi-step process remember that the following components are endothermic; enthalpy of sublimation, bond dissociation energy, ionization energy. The components that are exothermic are; electron affinity (usually) and lattice energy. Don't forget that the standard enthalpy of formation is for 1 mole of the substance. The Born-Haber process is just a special case of Hess's Law: *The heat of a reaction is constant, whether the reaction is carried out directly in one step or indirectly through a number of steps.*

Molecular Bonding: Writing Lewis Dot Structures

1. The valence electrons of all atoms are added together.
2. If the substance is a polyatomic ion, we must take into account the electrons used to form the ion. For anions, the charge represents additional electrons that must be added to the total of the valence electrons. For cations, the charge represents missing electrons that must be subtracted from the valence electrons.
3. A pair of electrons is placed between each two atoms in the skeletal structure to represent a covalent bond. These electrons are called the **bonding pairs**. Sometimes a line is used between the atoms to represent a pair of electrons.
4. The remaining electrons are used to complete the octets of all outer atoms in the skeleton. These electrons are **nonbonding pairs** of electrons (also called **lone pairs**).
5. If any electrons are left over, they are added in pairs to the central atom. These electrons are also nonbonding pairs (lone pairs).
6. When all electrons have been placed, the outer atoms will all have octets. The central atom may have an octet, or it may have more or fewer than eight electrons.
 - a. If the central atom has an octet, the structure is complete (see section on "most probable" Lewis structures for more information).
 - b. It is all right if boron, as a central atom, has fewer than eight electrons (it often has six). For other central atoms, double or triple bonds must be constructed to obtain an octet. This is done by taking nonbonding pairs of electrons from outer atoms and placing them as a bonding pairs. Enough bonds are constructed to give the central atom an octet. (**Note:** The *maximum* number of electrons between atoms is three, constituting a triple bond. See the section on *Determining the Most Probable Lewis Structure* to help identify the most appropriate configuration).

c. The central atom may have more than eight electrons (as in PCl_5) only if it is in periods 3A-7A on the periodic table. If the central atom is in *period* 2 (not group 2), it cannot have more than an octet of electrons.

Helpful Hints regarding Lewis Dot Structures:

1. Carbon is usually a central atom in the structure. In compounds with more than one carbon atom, the carbon atoms are joined in a chain to start the skeleton.
2. Hydrogen is never a central atom because it can form only one covalent bond (i.e. there is no 1p sublevel to fill).
3. Halogens form only a single covalent bond when oxygen is not present, and therefore a halogen will generally not be a central atom.
4. Oxygen forms only two covalent bonds and is rarely a central atom. However, it may link two carbon atoms in a carbon chain (as in the case of an ether $\text{R-O-R}'$, etc.).
5. In the simpler molecules, the atom that appears only once in the formula will be the central atom.

Determining the Most Probable Lewis Structure:

Recall:

Formal Charge = total number of valence electrons in the free atom - total number of nonbonding electrons - $\frac{1}{2}$ (total number of bonding electrons)

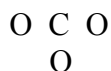
1. For neutral molecules, the sum of the formal charges must add up to zero (This rule applies, for example, to the O_3 molecule.)
2. For cations, the sum of the formal charges must equal the positive charge.
3. For anions, the sum of the formal charges must equal the negative charge.

If more than one potentially valid Lewis dot structure is possible for a compound, the following rules based on formal charge can help determine the most likely structure:

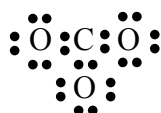
1. For neutral molecules, a Lewis structure in which the formal charges are zero is preferable to one in which formal charges are nonzero.
2. Lewis structures with large formal charges (± 2 , ± 3 , and so on) are less plausible than those with small formal charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Example: Determine the most plausible Lewis structure for CO_3^{2-} .

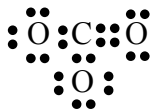
1. Based on rules of arrangement with the lowest electronegative element in the center, the skeletal structure is



2. The number of valence electrons available is 4 for carbon, 3 x 6 for oxygen and 2 more for the 2⁻ charge on the ion for a total of 24e⁻.
3. Creating bonds between the oxygens and the carbon, then filling in the octets for the oxygen we get



This is a problem since carbon doesn't have an octet, so we swing a pair of electrons from around the outside of one of the oxygen atoms (it doesn't matter which one), creating a double bond between it and the carbon.



Notice that the double bond is valid between the carbon and any of the oxygens. Because of the symmetry of this situation, the molecule is said to exhibit **resonance**. The reality of the situation is that the second bond is shared equally across all three carbon-oxygen bonds as a pair of **delocalized** electrons. The **bond order** is said to be $1 \frac{1}{3}$ because each bond "sees" $1 \frac{1}{3}$ bonds. See the section on resonance for more details.

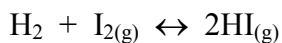
Strength of the Covalent Bond - Bond Energy:

The **bond dissociation energy** or **bond energy** is the enthalpy change (energy change at fixed pressure) required to break a particular bond in one mole of gaseous molecules. The symbol is designated by ΔH° . Since bond energies between two particular atoms can vary slightly from bond to bond, the average bond energy is normally listed in tables.

Using bond energies a person can get a reasonable idea of the energy of a reaction and whether or not the reaction is endothermic (indicated by a positive enthalpy) or exothermic (negative enthalpy). The reaction enthalpy is given by:

$$\Delta H^\circ = \Sigma \text{BE}(\text{reactants}) - \Sigma \text{BE}(\text{products})$$

where Σ represents the sum of the bond energies for the reaction. Remember that with reactants you are breaking bonds (endothermic) and with products you are forming bonds (exothermic). As an example consider



$$= 1x(\text{H}_2) + 1x(\text{I}_2) \leftrightarrow 2x(\text{HI})$$

$$= (1x436.4\text{kJ/mol}) + (1x151.0\text{kJ/mol}) - (2x298.3\text{kJ/mol}) = 436.4 + 151.0 - 596.6\text{kJ/mol}$$

$$= -9.2\text{kJ/mol}$$

Note the units of kJ/mol. This reaction is overall exothermic.